

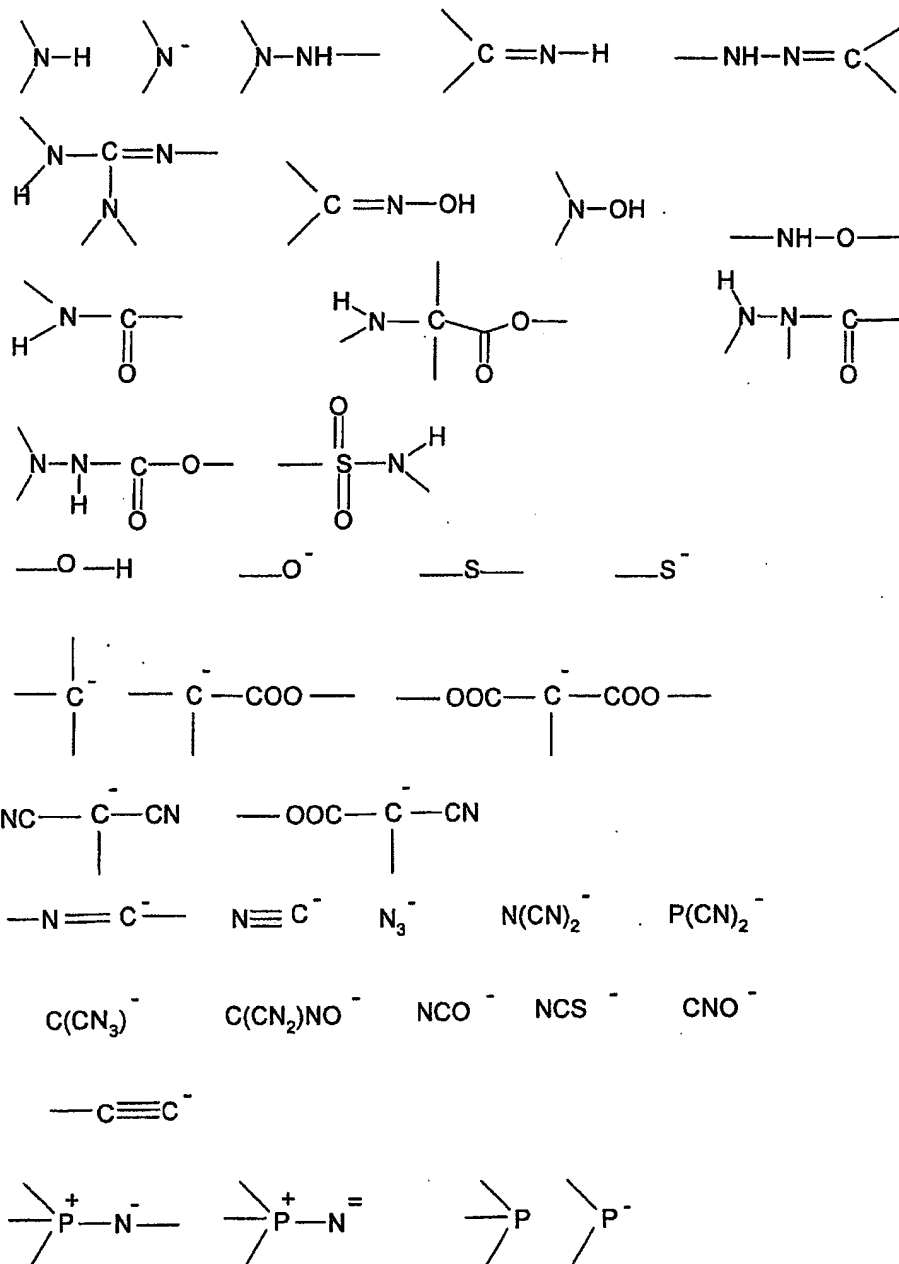
CLAIMS

1. A method for creating a carbon-carbon or carbon-heteroatom bond by the reaction of an unsaturated  
5 compound carrying a leaving group and a nucleophilic compound donating a carbon atom or a heteroatom (HE) capable of substituting for the leaving group, thus creating a C-C or C-HE bond, in the presence of a copper-based catalyst and a base, characterized in that  
10 the reaction takes place in the absence of a ligand and in a nitrile-type solvent.

2. The method as claimed in claim 1, characterized in that the nucleophilic substrate is an organic  
15 hydrocarbon compound which may be acyclic or cyclic and whose characteristic is to comprise at least one atom carrying a free doublet which may or may not comprise a charge, and preferably a nitrogen, oxygen, sulfur, phosphorus or carbon atom.

20

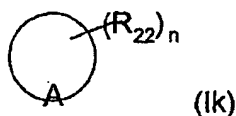
3. The method as claimed in either of claims 1 and 2, characterized in that the nucleophilic substrate comprises at least one atom or group below:



4. The method as claimed in one of claims 1 to 3,  
 5 characterized in that the nucleophilic substrate  
 comprises at least one nitrogen atom carrying a free  
 doublet contained in a saturated, unsaturated or  
 aromatic ring: the ring generally comprising from 3 to  
 8 atoms.
- 10
5. The method as claimed in claim 2, characterized in

that the nucleophilic substrate is a primary or secondary amine; an imine; an oxime; a hydroxylamine; a hydrazine; a hydrazone; an amide; a sulfoamide; a urea derivative; an amino acid; a heterocyclic derivative,  
5 preferably containing nitrogen and/or sulfur and/or phosphorus.

6. The method as claimed in claim 2, characterized in that the nucleophilic substrate corresponds to the  
10 following formula:



in said formula (Ik):

- A symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic, aromatic or  
15 nonaromatic heterocyclic system in which one of the carbon atoms is replaced by at least one nucleophilic atom such as a nitrogen, sulfur or phosphorus atom,
- $R_{22}$ , which are identical or different, represent  
20 substituents on the ring,
- n represents the number of substituents on the ring.

7. The method as claimed in claim 6, characterized in  
25 that the nucleophilic substrate corresponds to formula (Ik) in which A represents a ring such as: imidazole, pyrazole, triazole, pyrazine, oxadiazole, oxazole, tetrazole, indole, pyrrole, phthalazine, pyridazine, oxazolidine.

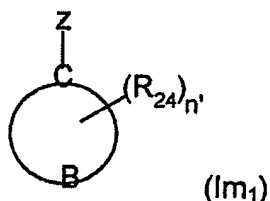
30

8. The method as claimed in claim 2, characterized in that the nucleophilic substrate is a compound of the alcohol or thiol type, preferably a compound of the hydroxy or thioaromatic type.

35

9. The method as claimed in claim 8, characterized in

that the nucleophilic substrate corresponds to the following formula:



in which:

- 5    -    B symbolizes the residue of a monocyclic or polycyclic aromatic carbocyclic group or a divalent group consisting of a succession of two or more monocyclic aromatic carbocyclic groups,
- $R_{24}$  represents one or more substituents which are
- 10    identical or different,
- Z represents a group of the  $OM_1$  or  $SM_1$  type in which  $M_1$  represents a hydrogen atom or a metal cation, preferably an alkali metal cation,
- $n'$  is a number less than or equal to 5.

15

10. The method as claimed in claim 2, characterized in that the nucleophilic substrate is a hydrocarbon compound comprising a nucleophilic carbon, preferably a malonate, a cyanomalonate, a malodinitrile, a compound comprising a cyanide anion or its generator, an acetylenide, a compound of the profen type, a nucleophilic compound comprising a carbanion and whose counter-ion is a metal, preferably lithium, sodium, magnesium or zinc.

25

11. The method as claimed in claim 2, characterized in that the nucleophilic substrate is a phosphide, a phosphine, a phosphonium azayldiide, a phosphonium azaylide.

30

12. The method as claimed in one of claims 1 to 11, characterized in that the nucleophilic compound is chosen from: pyrazole, oxazolidin-2-one, phenyl-

sulfonamide, 3,5-dimethylphenol, dimethyl or diethyl malonate.

13. The method as claimed in one of claims 1 to 12, characterized in that the compound carrying a leaving group Y is symbolized by the formula (II):

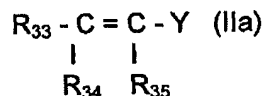


in said formula (II):

- $R_0$  represents a hydrocarbon group comprising from 2 to 20 carbon atoms and possesses a double bond at the  $\alpha$ -position with respect to a leaving group Y or a monocyclic or polycyclic aromatic carbocyclic and/or heterocyclic group carrying a leaving group Y on a ring.
14. The method as claimed in claim 13, characterized in that the compound comprising a leaving group corresponds to formula (II) in which:
- $R_0$  represents an aliphatic hydrocarbon group comprising a double bond at the  $\alpha$ -position with respect to the leaving group or an unsaturated cyclic hydrocarbon group in which an unsaturation carries the leaving group,
  - $R_0$  represents a monocyclic or polycyclic aromatic carbocyclic and/or heterocyclic group,
  - Y represents a leaving group, preferably a halogen atom or a sulfonic ester group of formula  $-\text{OSO}_2-\text{R}_e$ , in which  $\text{R}_e$  is a hydrocarbon group.
15. The method as claimed in either of claims 13 and 14, characterized in that the compound comprising a leaving group corresponds to formula (II) in which Y represents a bromine or chlorine atom or a sulfonic ester of formula  $-\text{OSO}_2-\text{R}_e$ , in which  $\text{R}_e$  is a linear or branched alkyl group having from 1 to 4 carbon atoms, preferably a methyl or ethyl group, a phenyl or tolyl group or a trifluoromethyl group.

16. The method as claimed in one of claims 13 to 15, characterized in that the compound comprising a leaving group corresponds to formula (II) and is chosen from the following compounds:

- (1) those of the aliphatic type carrying a double bond which may be represented by the formula (IIa):



10 in said formula (IIa):

- R<sub>33</sub>, R<sub>34</sub> and R<sub>35</sub>, which are identical or different, represent a hydrogen atom or a hydrocarbon group having from 1 to 20 carbon atoms, which may be a saturated or unsaturated, linear or branched aliphatic group; a monocyclic or polycyclic, saturated, unsaturated or aromatic carbocyclic or heterocyclic group; a succession of aliphatic and/or carbocyclic and/or heterocyclic groups as mentioned above,
- Y symbolizes the leaving group as defined above,
- (2) those of the aromatic type which are designated, in the text which follows, by "halo-aromatic compound" and which may be represented by the formula (IIb)

- Y represents a leaving group as defined above,
- n" represents the number of substituents on the ring.

5 17. The method as claimed in one of claims 13 to 16,  
characterized in that the compound carrying a leaving  
group corresponding to formula (II) is chosen from:  
vinyl chloride, vinyl bromide,  $\beta$ -bromostyrene,  
10  $\beta$ -chlorostyrene, bromobenzene, iodobenzene, p-chloro-  
toluene, p-bromoanisole, p-bromotrifluorobenzene.

18. The method as claimed in one of claims 13 to 17,  
characterized in that the compound carrying a leaving  
group corresponding to formula (II) is chosen from:  
15 bromobenzene and iodobenzene.

19. The method as claimed in one of claims 1 to 18,  
characterized in that the reaction takes place in the  
presence of a base.

20 20. The method as claimed in claim 19, characterized  
in that the base is chosen from: the carbonates,  
hydrogen carbonates or hydroxides of alkali metals,  
preferably of sodium, potassium or cesium, or of  
25 alkaline-earth metals, preferably calcium, barium or  
magnesium; alkali metal hydrides, preferably sodium  
hydride; alcoholates of alkali metals, preferably of  
sodium or potassium, and more preferably sodium  
methoxide, ethoxide or tert-butoxide; tertiary amines.

30 21. The method as claimed in one of claims 1 to 20,  
characterized in that the reaction takes place in the  
presence of a solvent of the nitrile-type which  
corresponds to the following formula:

35  $R_h-CN$  (III)

in said formula (III):

- $R_h$  represents a hydrocarbon group comprising at

least one nitrile group, having from 1 to 24 carbon atoms, optionally substituted, which may be a saturated or unsaturated, linear or branched acyclic aliphatic group; a monocyclic or polycyclic, saturated, unsaturated or aromatic cycloaliphatic group; a saturated or unsaturated, linear or branched aliphatic group, carrying a cyclic substituent.

22. The method as claimed in claim 21, characterized in that the nitrile-type solvent is chosen from: aliphatic or aromatic nitriles, preferably acetonitrile, propionitrile, butanenitrile, isobutanenitrile, pentanenitrile, 2-methylglutaronitrile, adiponitrile, benzonitrile, tolunitrile, malonitrile, 1,4-benzonitrile.

23. The method as claimed in claim 22, characterized in that the nitrile-type solvent is acetonitrile.

24. The method as claimed in one of claims 1 to 23, characterized in that the temperature for the arylation or vinylation reaction is between 0°C and 120°C, preferably between 20°C and 100°C, and more preferably still between 25°C and 85°C.

25. The method as claimed in one of claims 1 to 24, characterized in that the copper catalyst is chosen from: copper(I) bromide, copper(II) bromide, copper(I) iodide, copper(I) chloride, copper(II) chloride, basic copper(II) carbonate, copper nitrate, copper nitrate, copper sulfate, copper sulfate, copper(I) sulfite, copper(I) oxide, copper(II) oxide, copper(I) acetate, copper(II) acetate, copper(II) trifluoromethylsulfonate, copper(II) hydroxide, copper(I) methoxide, copper(II) methoxide, chlorocopper(II) methoxide or formula  $\text{ClCuOCH}_3$ .



26. The method as claimed in claim 25, characterized in that the copper catalyst is chosen from copper(I) or copper(II) chloride or bromide or iodide and copper(I) or copper(II) oxide.

5

27. The method as claimed in one of claims 1 to 26, characterized in that the catalyst is copper(I) iodide.

28. The method as claimed in claim 1, characterized in  
10 that the quantity of catalyst used, expressed by the molar ratio between the number of moles of copper catalyst expressed as copper and the number of moles of compound carrying the leaving group varies between 0.001 and 0.2, preferably between 0.01 and 0.1.

15

29. The method as claimed in claim 1, characterized in that the quantity of nitrile-type solvent to be used is determined such that the concentration of the compound carrying the leaving group in the organic solvent is  
20 between 0.5 and 2 mol/liter of organic solvent.